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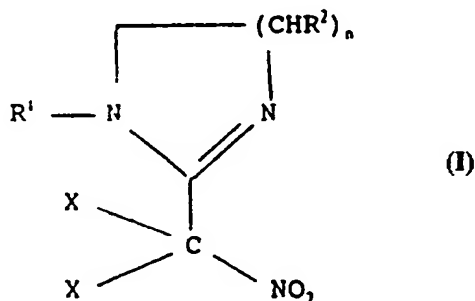
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<p>(21) International Application Number: PCT/EP94/01089 (22) International Filing Date: 6 April 1994 (06.04.94) (30) Priority Data: 93302748.4 7 April 1993 (07.04.93) EP (34) Countries for which the regional or international application was filed: GB et al. (71) Applicant: SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V. [NL/NL]; Carel van Bylandtlaan 30, NL-2596 HR The Hague (NL). (72) Inventors: MUNRO, David; 139 London Road, Maidstone, Kent ME16 0HF (GB). PATEL, Bipin; 89 Canterbury Road, Sittingbourne, Kent ME10 4JA (GB). (74) Agent: ALLAM, Peter, Clerk; Lloyd Wise, Tregear & Co., Norman House, 105-109 Strand, London WC2 0AE (GB).</p>		<p>(81) Designated States: AU, BR, CA, CN, HU, JP, KR, KZ, RU, UA, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published With international search report.</p>

(54) Title: DIHALONITROMETHYL HETEROCYCLES AND THEIR USE AS PESTICIDES

(57) Abstract

Nitromethyl compounds of general formula (I) wherein n is 1 or 2; R¹ represents an optionally substituted 3-pyridyl group; the group R² (when n is 1) is selected from, or each group R² (when n is 2) is independently selected from, an alkyl group, a haloalkyl group or a hydrogen atom; and each X independently represents a halogen atom; and processes for their preparation and their uses as pesticides are described.



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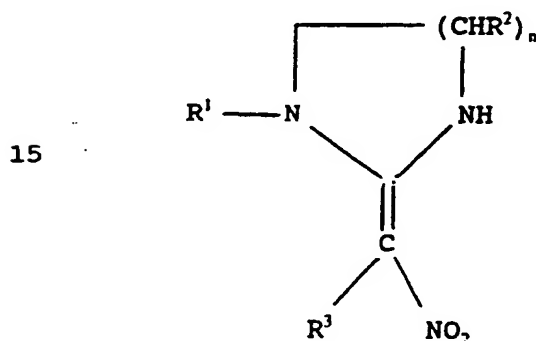
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DIHALONITROMETHYL HETEROCYCLES AND THEIR USE AS PESTICIDES

5 This invention relates to nitromethyl compounds, to processes for their preparation and to the use of such compounds as pesticides.

European Patent Application No. 0 369 526 (Shell)
 10 discloses nitromethylene compounds of general formula

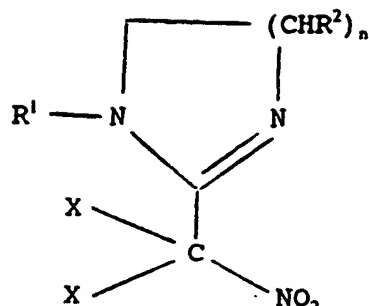


wherein n is 1, 2 or 3; R¹ is an optionally substituted 3-pyridyl group; each R² is independently selected from an alkyl group, a haloalkyl group or a hydrogen atom; and R³ is a hydrogen atom or an alkyl carbonyl group.

25 This invention is based on the discovery of a novel class of nitromethyl compounds which exhibit pesticidal activity.

30 According to the present invention, there is provided nitromethyl compounds of general formula

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I

15 wherein n is 1 or 2; R¹ represents an optionally substituted 3-pyridyl group; the group R² (when n is 1) is selected from, or each group R² (when n is 2) is independently selected from, an alkyl group, a haloalkyl group or a hydrogen atom; and each X independently represents a halogen atom.

20 Unless otherwise stated in this specification, when a group is designated as being optionally substituted, the substituent groups which are optionally present may be any of those customarily employed in the development of pesticidal compounds, and/or the modification of such compounds to influence their structure/activity, persistence, penetration or other property.

25 Examples of optional substituents of a 3-pyridyl group include halogen atoms and alkyl, alkoxy, alkylthio, haloalkyl, cyano, alkoxycarbonyl, alkylamino, dialkylamino, (alkylcarbonyl)alkylamino, (alkoxycarbonyl)-alkylamino, alkylcarbonylamino and alkoxycarbonylamino groups. Any alkyl moiety in such substituents is preferably C₁₋₆ alkyl, more preferably C₁₋₄ alkyl. Suitably the pyridyl group may have two, or, most preferably, one substituent.

35

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Included within the scope of the present invention are salts, for example quaternary salts, and N-oxides.

R¹ is preferably a 3-pyridyl group substituted in the
5 6-position by a halogen atom, a C₁₋₄ alkoxy group, a C₁₋₄ alkylthio group, a C₁₋₄ haloalkyl group, a cyano group or a (C₁₋₄ alkoxy)carbonyl group, more preferably a 3-pyridyl group substituted in the 6-position by a chlorine or
10 bromine atom, a methoxy group, a di- or trifluoromethyl group, or a cyano group. Advantageously, R¹ is a 6-halo-3-pyridyl group, most preferably 6-chloro-3-pyridyl, or 6-methoxy-3-pyridyl.

Unless otherwise stated in this specification, an
15 alkyl or alkenyl group may be linear or branched and suitably contains up to 10, preferably up to 6, and most preferably up to 4, carbon atoms, preferred examples being methyl and ethyl. Unless otherwise stated, a halogen atom
20 may suitably be a fluoride, bromine or, particularly suitably, a chlorine atom.

Alkyl moieties present in groups represented by R² are preferably C₁₋₄ alkyl, more preferably C₁₋₄ alkyl, with methyl and ethyl being especially preferred. Whilst any of the
25 moieties represented by R² in the -(CHR²)_n- group in compounds of formula I in which n is 2 may be alkyl or haloalkyl, it is preferred that alkyl or haloalkyl moieties represented by R² in such compounds are attached
30 to carbon atoms having an adjacent nitrogen atom. Each R² is most preferably a hydrogen atom.

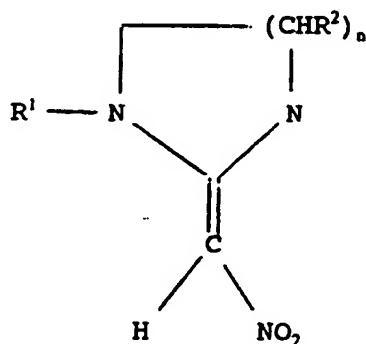
To date the most promising activity has been found in compounds of formula I in which n is 2.

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Preferably both groups X are identical to one another. Suitably they are both bromine or, most preferably, both chlorine atoms.

5 The invention further provides a process for the preparation of a compound of general formula I as defined above which comprises treating a compound of general formula

10



15

II

20 with a halogenating agent wherein in the compound of general formula II, n, R¹ and R², are as described above.

A suitably halogenating agent may be a halogen gas or, more preferably, a N-halosuccinimide, for example N-bromosuccinimide or N-chlorosuccinimide. A base may be present, for example an alkali metal base, preferably sodium carbonate.

25 The reaction is preferably carried out at a temperature in the range 10° to 60°C, more preferably, at ambient temperature, suitably with stirring.

30 The reaction is preferably carried out in the presence of an inert organic solvent. Halogenated hydrocarbons, for example carbon tetrachloride, are

35

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suitable. After subsequent removal of the solvent, the desired product may be isolated by standard procedures.

Compounds of general formula II may be prepared as described in European Patent Application No 0 369 526 (Shell).

The compounds of general formula I exhibit pesticidal, particularly insecticidal, activity. Accordingly, the invention also provides a pesticidal composition comprising a carrier and, as active ingredient, a compound of general formula I. The invention further provides a method of combating pests at a locus, which comprises treating the locus with a pesticidal compound or composition according to the invention, and specifically provides the use as an insecticide of a compound of general formula I.

Particularly interesting activity has been observed against Sternorrhynchus and Auchenorrhynchus insects. Preferred aspects of the present invention therefore relate to the pesticidal treatment of such pests. A particularly preferred aspect of the present invention relates to the pesticidal treatment of plant and leaf hoppers.

A carrier in a composition according to the invention is any material with which the active ingredient is formulated to facilitate application to the locus to be treated, which may for example be a plant, seed or soil, or to facilitate storage, transport or handling. A carrier may be a solid or a liquid, including a material which is normally gaseous but which has been compressed to form a liquid, and any of the carriers normally used in formulating pesticidal compositions may be used.

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Preferably compositions according to the invention contain 0.5 to 95% by weight of active ingredient.

Suitable solid carriers include natural and synthetic
5 clays and silicates, for example natural silicas such as diatomaceous earths; magnesium silicates, for example talcs; magnesium aluminium silicates, for example attapulgites and vermiculites; aluminium silicates, for example kaolinites, montomorillonites and micas; calcium
10 carbonate; calcium sulphate; ammonium sulphate; synthetic hydrated silicon oxides and synthetic calcium or aluminium silicates; elements, for example carbon and sulphur; natural and synthetic resins, for example coumarone resins, polyvinyl chloride, and styrene polymers and
15 copolymers; solid polychlorophenols; bitumen; waxes; and solid fertilisers, for example superphosphates.

Suitable liquid carriers include water; alcohols, for example isopropanol and glycols; ketones, for example
20 acetone, methyl ethyl ketone, methyl isobutyl ketone and cyclohexanone; ethers; aromatic or araliphatic hydrocarbons, for example benzene, toluene and xylene; petroleum fractions, for example kerosine and light mineral oils; chlorinated hydrocarbons, for example carbon
25 tetrachloride, perchloroethylene and trichloroethane. Mixtures of different liquids are often suitable.

Agricultural compositions are often formulated and transported in a concentrated form which is subsequently
30 diluted by the user before application. The presence of small amounts of a carrier which is a surface-active agent facilitates this process of dilution. Thus, preferably at least one carrier in a composition according to the invention is a surface-active agent. For example the

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composition may contain at least two carriers, at least one of which is a surface-active agent.

A surface-active agent may be an emulsifying agent, a dispersing agent or a wetting agent; it may be nonionic or ionic. Examples of suitable surface-active agents include the sodium or calcium salts of polyacrylic acids and lignin sulphononic acids; the condensation products of fatty acids or aliphatic amines or amides containing at least 12 carbon atoms in the molecule with ethylene oxide and/or propylene oxide; fatty acid esters of glycerol, sorbitan, sucrose or pentaerythritol; condensates of these with ethylene oxide and/or propylene oxide; condensation products of fatty alcohol or alkyl phenols, for example p-octylphenol or p-octylcresol, with ethylene oxide and/or propylene oxide; sulphates or sulphonates of these condensation products; alkali or alkaline earth metal salts, preferably sodium salts, of sulphuric or sulphononic acid esters containing at least 10 carbon atoms in the molecule, for example sodium lauryl sulphate, sodium secondary alkyl sulphates, sodium salts of sulphonated castor oil, and sodium alkylaryl sulphonates such as dodecylbenzene sulphonate; and polymers of ethylene oxide and copolymers of ethylene oxide and propylene oxide.

The compositions of the invention may for example be formulated as wettable powders, dusts, granules, solutions, emulsifiable concentrates, emulsions, suspension concentrates and aerosols. Wettable powders usually contain 25, 50 or 75% w of active ingredient and usually contain in addition to solid inert carrier, 3-10% w of a dispersing agent and, where necessary, 0-10% w of stabiliser(s) and/or other additives such as penetrants or stickers. Dusts are usually formulated as a dust concentrate having a similar composition to that of a

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wettable powder but without a dispersant, and are diluted in the field with further solid carrier to give a composition usually containing $1/2$ -10% w of active ingredient. Granules are usually prepared to have a size
5 between 10 and 100 BS mesh (1.676 - 0.152 mm), and may be manufactured by agglomeration or impregnation techniques. Generally, granules will contain $1/2$ -75% w active ingredient and 0-10% w of additives such as stabilisers, surfactants, slow release modifiers and binding agents.
10 The so-called "dry flowable powders" consist of relatively small granules having a relatively higher concentration of active ingredient. Emulsifiable concentrates usually contain, in addition to a solvent and, when necessary, co-solvent, 10-50% w/v active ingredient, 2-20% w/v
15 emulsifiers and 0-20% w/v of other additives such as stabilisers, penetrants and corrosion inhibitors. Suspension concentrates are usually compounded so as to obtain a stable, non-sedimenting flowable product and usually contain 10-75% w active ingredient, 0.5-15% w of
20 dispersing agents, 0.1-10% w of suspending agents such as protective colloids and thixotropic agents, 0-10% w of other additives such as defoamers, corrosion inhibitors, stabilisers, penetrants and stickers, and water or an organic liquid in which the active ingredient is
25 substantially insoluble; certain organic solids or inorganic salts may be present dissolved in the formulation to assist in preventing sedimentation or as antifreeze agents for water.

30 Aqueous dispersions and emulsions, for example compositions obtained by diluting a wettable powder or a concentrate according to the invention with water, also lie within the scope of the invention. The said emulsions may be of the water-in-oil or of the oil-in-water type,
35 and may have a thick "mayonnaise"-like consistency.

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Compositions in accordance with the invention may also contain other ingredients, for example other compounds possessing pesticidal, herbicidal, or fungicidal properties. The compounds of the invention may be found to be especially useful when applied in admixture with other insecticides and/or acaricides, e.g. organophosphates, pyrethroids, ureas and organotin compounds, for example the commercial products fenvalerate, permethrin, cypermethrin, deltamethrin, alphacypermethrin, fenbutatin oxide, flufenoxuron diflubenzuron and trefluron.

The invention will be further understood from the following illustrative examples.

Example 1

Preparation of 1-(6-methoxy-3-pyridyl)-2-(dichloronitromethyl)-1,3-diazacyclohex-2-ene

[n = 2, R¹ = 6-methoxy-3-pyridyl, both groups R² = H, both groups X = Cl].

2 - Nitromethylene - 1 - (6 - methoxy - 3 - pyridyl)hexahydropyrimidine (6.7 g) prepared in accordance with methods described in EP 369526A, and N-chlorosuccinimide (3.8 g) were added to carbon tetrachloride and the reaction mixture was stirred at ambient temperature for 24 hours. Following an assessment by thin layer chromatography excess solvent was removed by evaporation, and the residue chromatographed (silica; eluent was 95% trichloromethane, 5% methanol). The product was collected as a brown solid (2.9 g). This was recrystallised from n-hexane and ethyl acetate. The melting point was 122-3°C (with decomposition).

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Analysis

	%C	%H	%N
Calc.	41.4	3.8	17.6
Found	41.7	4.1	17.2

5

Example 2Preparation of 1-(6-chloro-3-pyridyl)-2-(dibromonitromethyl)-1,3-diazapent-2-ene

[n = 1, R¹ = 6-chloro-3-pyridyl, R² = H, both groups
10 X = Br].

2-Nitromethylene-1-(6-chloro-3-pyridyl)imidazolidine
(1 g) prepared in accordance with methods described in EP
369526A, was added to carbon tetrachloride (30 ml) with
15 sodium carbonate (0.5 g), and bromine (1.5 g) was added
dropwise giving a temperature rise from 21°C to 35°C. The
reaction mixture was stirred overnight at ambient
temperature. The product was separated by thin layer
chromatography (silica; eluant was 90% trichloromethane,
20 10% methanol) to give a colourless solid (0.8 g). This
was recrystallised from ethyl acetate to give colourless
crystals. mp 160°C (with decomposition).

Analysis

	%C	%H	%N
Calc.	27.1	1.7	14.1
Found	27.5	2.1	13.8

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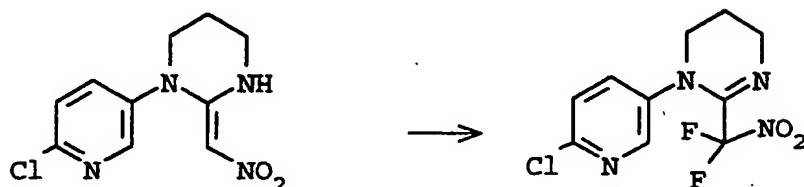
Examples 3 to 8

30 Further compounds as noted in Table 1 were prepared
by processes analogous to the processes of Examples 1 and
2. Characterising data for the compounds of Examples 3 to
8 is also noted in Table 1.

TABLE 1

Example No.	R'	X	-(CHR') _n -	mp°C	Analysis CHN wt% Calculated Found	
3	6-chloro-3-pyridyl	Cl, Cl	CH ₂	173	34.9 35.0	2.3 2.6 18.1 18.0
4	6-chloro-3-pyridyl	Cl, Cl	(CH ₂) ₂	158	37.1 36.5	2.8 2.9 17.3 16.7
5	6-bromo-3-pyridyl	Cl, Cl	CH ₂	168	30.5 30.3	2.0 2.3 15.8 15.6
6	6-bromo-3-pyridyl	Br, Br	CH ₂	149	24.4 24.2	2.0 1.8 12.6 12.5
7	6-bromo-3-pyridyl	Cl, Cl	(CH ₂) ₂	156	32.6 32.7	2.4 2.7 15.2 14.8
8	6-methoxy-3-pyridyl	Br, Br	CH ₂	114		

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EXAMPLE 9Preparation of 1-(6-chloro-3-pyridyl)-2-difluoronitromethyl)-1,3-diazacyclohex-2-ene

2-Nitromethylene-1-(6-chloro-3-pyridyl)hexahydro-pyrimidine prepared in accordance with the methods described in EP 369526A, and N-fluoro-2,4,6-trimethylpyridinium triflate (5g) are added to dichloromethane (25ml) and the reaction mixture is stirred overnight. Aqueous sodium carbonate (2.2g/20ml) is added and the organic layer is separated. Following an assessment by thin layer chromatography (Silica; eluent is 95% trichloromethane, 5% methanol), the fast moving component is collected as a colorless oil which solidifies (1.4g). This product is recrystallized to a colorless compound from n-hexane and ethyl acetate. The melting point of the compound is 133°C.

Analysis

	%C	%H	%N
Calc.	41.3	3.1	19.3
Found	41.2	3.2	19.4

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Example 10Preparation of 1-(6-chloro-3-pyridyl)-2-difluoro-nitrmethyl)-1,3-dizapent-2-ene

Following the procedures set forth in Examples 2 and 9, the title compound is prepared characterizing data for this compound (mp=137°C) is given below.

Analysis

	%C	%H	%N
Calc.	39.1	2.5	20.2
Found	38.6	2.7	19.5

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EXAMPLE 11Insecticidal Activity

5 Insecticidal activity of compounds of the invention was assessed against various of the following pests:-

Spodoptera littoralis (Egyptian cotton leafworm)

Aedes aegypti (yellow fever mosquito)

Musca domestica (housefly)

10 Acyrthosiphon pisum (pea aphid)

Trialeurodes vaporariorum (greenhouse whitefly)

Nephotettix cincticeps (green leaf hopper)

Plutella xylostella (diamond back moth)

15 The test methods employed for each species appear below. In each test, unless otherwise stated, solutions or suspensions of test compound were made up over a range of concentrations in water (initially 0.1%w) containing 10%w acetone and 0.025%w "TRITON X-100" (trade mark) surface
20 active agent (the condensation product of ethylene oxide with an alkyl phenol). These solutions were sprayed at a rate equivalent to 340 litres per hectare ($3.4 \times 10^{-4} \text{ m}^3/\text{m}^2$) onto Petri dishes containing either test species per se or diet onto which test species were subsequently introduced,
25 as indicated. In some assays leaf discs infested with test species were sprayed whilst other assays involved the spraying of plants which were infested subsequently with test species after the spray solution had dried. The tests were all conducted under normal insectary conditions ($23^\circ\text{C} \pm 2^\circ\text{C}$, fluctuating humidity and light). Mortality
30 assessments were made as indicated below, in terms of percentage mortality figures. Thus, a LC_{50} (the dosage of active material required to kill half of the test species) for the compound was calculated from the mortality figures
35 and compared with the corresponding LC_{50} for a standard

- 15 -

insecticide, ethyl parathion, in the same test. The results are expressed as toxicity indices thus:

$$\text{toxicity index} = \frac{\text{LC}_{50} (\text{parathion})}{\text{LC}_{50} (\text{test compound})} \times 100$$

(i) Spodoptera littoralis (1 and 7 day) (S1 1D : S1 7D)

Test solutions were sprayed as indicated above onto Petri dishes containing a nutritious diet for Egyptian cotton leafworm larvae. When the spray deposit had dried, each dish was infested with ten 2nd instar larvae. Mortality assessments were made 1 day and 7 days after spraying.

(ii) Aedes aegypti (Aa)

Early 4th instar larvae were used. Test solutions were made up to 0.5 ppm of test compound (and progressive half-dilutions) in water containing 0.04%w "TRITON X-100" (trade mark); acetone was initially present to aid solution, but was allowed to evaporate off before introduction of larvae.

Ten early 4th instar larvae were placed in 100 ml of test solution held at 28°C, and after 48 hours, larval mortality was recorded. The final mortality was assessed by counting the number of emerged adult mosquitoes after one week.

(iii) Musca domestica (Md)

Batches of ten 2 to 3 day old milk-fed adult female houseflies, anaesthetised using carbon dioxide, were placed on filter papers inside Petri dishes. The dishes were sprayed with the test solutions as described above. The flies were retained in the Petri dishes and were fed with a dilute milk solution which was dripped down the side of

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the Petri dish and absorbed by the filter paper. Mortality was assessed after 24 hours.

(iv) Acyrtosiphon pisum (Ap)

5 Tests were carried out on young adult pea aphids. Whole pea plants 6 days after germination were placed on filter papers in Petri dishes. Ten aphids were transferred to each pea plant and left for 30 minutes to allow the aphids to settle and start to feed. The dishes were then
10 sprayed with the test solutions as described above and lids were placed on the Petri dishes. Mortality was assessed after 24 hours.

(v) Trialeurodes vaporariorum (Tv)

15 French bean plants (Phaseolus vulgaris) with two fully expanded leaves were placed in a breeding culture of T. vaporariorum, also on French bean plants, which were then disturbed to ensure resettlement on the introduced plants. During the subsequent 24 hour period, eggs were deposited
20 and kept at 27°C, with 14 hours photoperiod. All adult whiteflies were then carefully removed, leaving egg samples of a known age. After eight days the majority of eggs had hatched. Leaf discs containing the newly hatched nymphs were then cut from the leaves and transferred to moist
25 filter paper. The discs were examined under a low-powered microscope to determine the exact number of 1st instar nymphs per disc and to remove any unhatched eggs. On average, 70-100 nymphs were found per disc.

30 The discs were transferred into Petri dishes and sprayed with test solutions as described above. After 6 days percentage mortalities were assessed.

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(vi) Nephotettix cincticeps (Nc)

Tests were carried out on young adult female green leaf
hoppers. Plant pots, each containing five rice seedlings
10 to 15 cm tall arranged across the centre of the pot, were
5 sprayed with test solutions as described above (but initial
test concentration 0.05% of test compound). Spraying was
on both sides of the plants with the pots horizontal. One
hour after spraying, each pot was filled to the brim with
fine silver sand, an open-ended glass jar was placed over
10 each pot and each pot was infested with ten hoppers. A
paper tissue was placed over the open end of each glass jar
to retain the hoppers. The pots were irrigated from
underneath, maintained at a temperature of $27^{\circ}\text{C} \pm 2^{\circ}\text{C}$ and
subjected to white fluorescent light under a regime of 18
15 hours light followed by 6 hours darkness. Mortality
assessments were made 48 hours after infestation.

(vii) Plutella xylostella (Px)

A test solution was sprayed as described above onto a
20 4 cm diameter Chinese cabbage leaf placed ventral side up
in a pot. When the spray deposit had dried the pot was
infested with 10 young instar larvae and a lid added.
Mortality was assessed after 1 or 2 days, depending on when
the test was carried out.

25

EXAMPLE 12Acaricidal Activity (ovicide) (Tu OA)

Acaricidal activity of the compounds of Examples 1 to
30 8 was assessed, employing eggs of the glasshouse red spider
mite, Tetranychus urticae (T.u.), less than 24 hours old,
by the following procedure.

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2cm diameter leaf discs cut from the leaves of French bean plants were placed on filter paper, kept moist by a cotton wool wick dipped into water.

5 On the day before spraying, each leaf disc was infested with 10 female adult mites. On the day of the test, the adults were removed, leaving the eggs laid overnight on the discs. The leaf discs were then sprayed with solutions of test compound made up as in Example 9 above, at a rate
10 equivalent to 340 litres per hectare ($3.4 \times 10^{-5} \text{ m}^3/\text{m}^2$).

Throughout the test, the eggs were held under normal insectary conditions ($23^\circ\text{C} \pm 2^\circ\text{C}$, fluctuating humidity and 16 hours days length). After 7-10 days, the numbers of
15 hatched nymphs and unhatched eggs were assessed and the percentage mortality calculated. The LC_{50} (the dosage of active material required to kill half of the test species) for the compound was calculated from the mortality figure and compared with the corresponding LC_{50} for a standard
20 insecticide, chlorfenson, in the same test. The result is expressed as toxicity index thus:

$$\text{toxicity index} = \frac{\text{LC}_{50} (\text{chlorfenson})}{\text{LC}_{50} (\text{test compound})} \times 100$$

25

Results of the assessments described in Examples 9 and 10 for each of the compounds of Examples 1 to 8 are provided in Table 2. In Table 2 a blank square indicates that testing was not carried out. The letters B and C indicate
30 that the first test carried out at the initial test concentration of 0.1%wt (1000 ppm) gave a mortality assessment of 40-69% and 0-39%, respectively. When that initial test yielded a mortality assessment of 70-100%, a rating of A would be given. Usually further testing to

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yield toxicity indices as described above was then carried out. Toxicity indices are stated, where available.

Results are also given for comparison compounds C1 and
5 C2. Compound C1 is 2-nitromethylene-1-(6-chloro-3-pyridyl)imidazolidine (Ex. 8 of EP 369526A). Compound C2 is 2-nitromethylene-1-(6-chloro-3-pyridyl)hexahydropyrimidine (Ex. 7 of EP 369526A). Thus, they enable direct comparisons to be made with Examples 3 and 4 respectively, of the
10 present invention.

It will be observed that Examples 3 and 4 of the present invention show very high activity against green leaf
hoppers, very much higher than the activity, itself
15 substantial, shown by comparison compounds C1 and C2.

TABLE 2

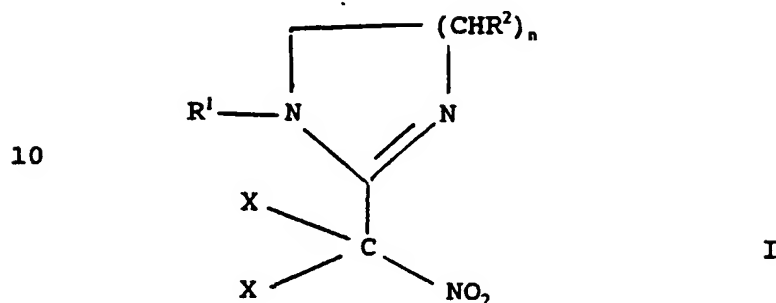
Compound of Example	Toxicity Indices									
	Sl 1D - Sl 7D	Aa	Md	Ap	Tv	Nc	Tu OA	Px		
1	C	C	A	C						
2	C	9	7	4	21	290	>28	A		
3	C	C	7	C	C	12000	C			
4	C	C	27	C	2	28000	C			
5	C	C	A	B	A		C	A		
6	C	A	C	C	A		C	A		
7		7			C	8200		C		
8	C	C	C	C	A		C	A		
C1	19	45	6	710	450	3700	C			
C2	C	130	3	110	1100	3200	C			

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CLAIMS

1. A compound of general formula

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wherein n is 1 or 2; R^1 represents an optionally substituted 3-pyridyl group; the group R^2 (when n is 1) is selected from, or each group R^2 (when n is 2) is independently selected from, an alkyl group, a haloalkyl group or a hydrogen atom; and each X independently represents a halogen atom.

2. A compound as claimed in claim 1, wherein R^1 is a 3-pyridyl group substituted in the 6-position by a halogen atom, a C_{1-4} alkoxy group, a C_{1-4} alkylthio group, a C_{1-4} haloalkyl group, a cyano group or a (C_{1-4} alkoxy)carbonyl group.

3. A compound as claimed in claim 1 or claim 2, wherein R^2 represents a hydrogen atom.

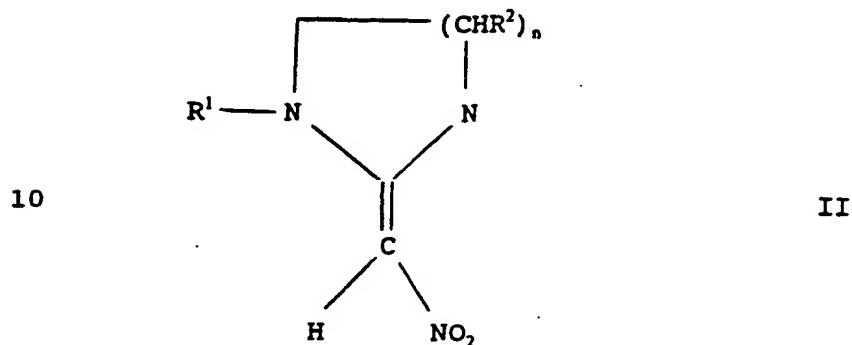
4. A compound as claimed in any preceding claim, wherein both groups X represent bromine atoms or both groups X represent chlorine atoms or both groups X represent fluorine atoms.

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5. A process for the preparation of a compound of general formula I as claimed in any preceding claim which comprises treating a compound of general formula

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with a halogenating agent wherein in the compound of general formula II, n , R^1 and R^2 , are as claimed in any preceding claim.

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6. A compound as claimed in any of Claims 1 to 4, when prepared by a process as claimed in Claim 5.

7. A pesticidal composition comprising a carrier and, as active ingredient, a compound of general formula I as claimed in any of Claims 1 to 4 or Claim 6.

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8. A method of combating pests at a locus, which comprises treating the locus with a pesticidal compound or composition as claimed in any of Claims 1 to 4, 6 or 7.

9. Use as an insecticide or as an acaricide of a compound or composition as claimed in any of Claims 1 to 4, 6 or 7.

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10. A compound, composition, process, method or use in accordance with the invention, substantially as hereinbefore described with reference to the Examples.

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/EP 94/01089

A. CLASSIFICATION OF SUBJECT MATTER

IPC 5 C07D401/04 A01N43/50 A01N43/54

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 5 C07D A01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP,A,0 369 526 (SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ) 23 May 1990 cited in the application see claims 1,8 ---	1,7
Y	EP,A,0 192 060 (NIHON TOKUSHU NOYAKU SEIZO) 27 August 1986 see page 193; claims 1,9 -----	1,7

☐ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier document but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
"&" document member of the same patent family

Date of the actual completion of the international search

13 July 1994

Date of mailing of the international search report

20.07.94

Name and mailing address of the ISA

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Authorized officer

Voyiazoglou, D

INTERNATIONAL SEARCH REPORT

Information on patent family members

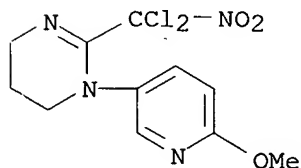
International application No.

PCT/EP 94/01089

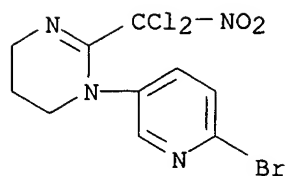
Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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		JP-A- 2180879	13-07-90
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L12 ANSWER 22 OF 102 CAPLUS COPYRIGHT 2003 ACS
 AN 1995:219295 CAPLUS
 DN 122:10060
 TI Preparation of 1-(3-pyridyl)-2-(dihalomitromethyl)-1,3-diazacyclopent-2-
 enes and -diazacyclohex-2-enes as pesticides.
 IN Munro, David; Patel, Bipin
 PA Shell Internationale Research Maatschappij B.V., Neth.
 SO PCT Int. Appl., 26 pp.
 CODEN: PIXXD2
 DT Patent
 LA English
 FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	WO 9422851	A1	19941013	WO 1994-EP1089	19940406
	W: AU, BR, CA, CN, HU, JP, KR, KZ, RU, UA				
	RW: AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE				
	AU 9465393	A1	19941024	AU 1994-65393	19940406
	ZA 9402392	A	19950116	ZA 1994-2392	19940407
PRAI	EP 1993-302748		19930407		
	WO 1994-EP1089		19940406		
OS	CASREACT 122:10060; MARPAT 122:10060				
AB	Title compds. [I; n = 1, 2; R1 = (substituted) 3-pyridyl group; R2 = H, alkyl, haloalkyl; X, X1 = halo], were prepd. Thus, 2-nitromethylene-1-(6-methoxy-3-pyridyl)hexahydropyrimidine was stirred with N-chlorosuccinimide in CCl4 for 24 h to give 1-(6-methoxy-3-pyridyl)-2-(dichloronitromethyl)-1,3-diazacyclohex-2-ene. I showed a toxicity index [[LC50 (parathion)/LC50 (I)] .times. 100] = 1000-28000 against Nephrotettix cincticeps.				
IT	159336-02-4P 159336-06-8P 159336-07-9P 159336-09-1P				
	RL: AGR (Agricultural use); BAC (Biological activity or effector, except adverse); BSU (Biological study, unclassified); SPN (Synthetic preparation); BIOL (Biological study); PREP (Preparation); USES (Uses) (prepn. of 2-(dihalomitromethyl)-1,3-diazacyclopent-2-enes and -diazacyclohex-2-enes as pesticides)				
RN	159336-02-4 CAPLUS				
CN	Pyrimidine, 2-(dichloronitromethyl)-1,4,5,6-tetrahydro-1-(6-methoxy-3-pyridinyl)- (9CI) (CA INDEX NAME)				

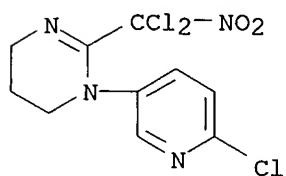


RN 159336-06-8 CAPLUS
 CN Pyrimidine, 1-(6-bromo-3-pyridinyl)-2-(dichloronitromethyl)-1,4,5,6-tetrahydro- (9CI) (CA INDEX NAME)



RN 159336-07-9 CAPLUS

CN Pyrimidine, 1-(6-chloro-3-pyridinyl)-2-(dichloronitromethyl)-1,4,5,6-tetrahydro- (9CI) (CA INDEX NAME)



RN 159336-09-1 CAPLUS

CN Pyrimidine, 1-(6-chloro-3-pyridinyl)-2-(difluoronitromethyl)-1,4,5,6-tetrahydro- (9CI) (CA INDEX NAME)

